Thermopower of high-T_c cuprates

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We have studied the thermopower of La_2CuO_{4+z} and Nd_2CuO_{4-y} which undergo an antiferromagnetic transition near room temperature and $Bi_2Sr_{2-x}La_xCuO_{6+z}$ for which a broad spectrum of doping is possible. The thermopower of La_2CuO_{4+z} and Nd_2CuO_{4-y} is seen to exhibit an anomaly at the Neel temperature, whereas the resistivity is not. The extrapolated zero-temperature intercept of the thermopower, which is known to be positive for hole-doped cuprate superconductors, is found to become negative for $Bi_2Sr_{2-x}La_xCuO_{6+z}$ above some critical doping-level. The data strongly suggest that the thermopower of high-T_c cuprates contains a large amount of extra contribution in addition to the usual diffusion thermopower. We discuss origins of the extra contribution in the thermopower.

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The nature of the normal state of the high-T_c cuprate superconductors (HTSC) has remained a key issue since their discovery. The normal state exhibits a variety of anomalous electronic properties. The thermopower is one of several physical quantities which distinctly reveal the unusual normal-state properties. The ab-plane thermopower of hole-doped HTSC exhibits simple but unusual dependences on temperature and on the doping level. [1–3] At high temperatures, the thermopower S varies linearly in temperature T with a negative slope and a positive zero-offset (extrapolated zero-temperature intercept). The negative slope depends weakly on the doping level, while the zero offset varies from a large positive value at low doping-level to near zero in the overdoped region. The dependence of S on temperature and the doping level is so systematic and universal that it can be used as a measure of the hole concentration in the CuO_2 planes for any hole-doped HTSC. [1] Recent theoretical work [4] shows, based on the conventional Fermi-liquid model [5], that the doping-level dependence of the thermopower can be explained by the common band-dispersion-relation of HTSC. However there does not yet exist a plausible explanation for the unusual temperature-dependence of S, which is not easily reconciled with a conventional model based on the usual phonon-drag contribution and/or a multi-banded electronic-structure. The observed simplicity and universality in S seems to indicate that the electronic structure is simple and common to the all kinds of HTSC. Thermopower measurements on semiconducting and heavily-overdoped samples, S of which has not been studied in detail yet, may provide valuable informations for understanding the unusual T-dependence of S.

The present paper reports an investigation of S of La_2CuO_{4+z} and Nd_2CuO_{4-y} which are semiconducting and undergo an antiferromagnetic (AFM) transition below room temperature and $Bi_2Sr_{2-x}La_xCuO_{6+z}$ which enables the normal-state properties in the heavily-overdoped region to be studied down to below 20 K.

The conventional solid-state reaction of stoichiometric oxides and carbonates was adopted in preparing polycrystalline samples of La_2CuO_{4+z}, Nd_2CuO_{4-y}, and $Bi_2Sr_{2-x}La_xCuO_{6+z}$. The X-ray diffraction analysis shows all the samples to be single phase within the experimental error. S was measured by employing the dc method described in Ref. 6. S of the polycrystalline samples represents essentially the ab-plane value due to the relatively high conductivity in the CuO_2 planes as compared to that along the c axis. The resistivity was measured through the low-frequency ac four-probe method.

Fig. 1 shows the temperature dependence of S for semiconducting La_2CuO_{4+z} (LCO) and Nd_2CuO_{4-y} (NCO). Both samples show a distinct drop of $|S|$ at $\sim$150 K for LCO and at $\sim$260 K for NCO. The anomaly in S is associated with the AFM transition [7–9]. The onset of S drop for LCO was reported to appear at the same temperature where a sharp peak in the magnetic susceptibility appears. [10] The onset temperature of S drop for NCO as well coincides with the Neel temperature T_N in Ref. 11. The change of S in association with the AFM transition is as large as $\sim 50\%$ of S(300 K) for LCO at a moderate estimate. For NCO, it is $\sim 40\%$. Despite such distinct changes in S associated with the AFM transition, the resistivity measurements on the samples cut from the same pellets do *not* reveal any anomaly near T_N, as shown in Fig. 2. The absence of an anomaly at T_N in the resistivity has been observed in many different experiments on LCO and NCO samples. [12–15] In the relaxation-time approximation, the diffusion contribution S_d in S is related to the density of states, the velocity and the relaxation time of conduction electrons, and so is the resistivity ρ in a similar way. [5] Therefore, when S_d shows an anomaly at T_N, ρ is also expected to show a similar anomaly at the same temperature, as appeared in transition metals [5]. The absence of an anomaly at T_N in ρ of our samples strongly suggests that the observed large change in S might not be of S_d but of an extra contribution, either the excitation-drag thermopower or something else which is reduced in association of the AFM ordering.

Fig. 3 shows (a) S vs. T of $Bi_2Sr_{2-x}La_xCuO_{6+z}$ with

$0.1 \leq x \leq 0.9$ and (b) the dependence on the La-content x of the zero-offset S_o and the superconducting-transition temperature T_c. The temperature and doping dependence of S for the samples with $x > 0.4$ are typical of HTSC; linear in T with a negative slope and a positive S_o. The zero-offset S_o having a large positive value at large x falls to zero at $x \simeq 0.4$. Lowering x further below 0.4 (raising the hole concentration above 0.28), S_o becomes *negative*. The hole concentration of the sample of $x = 0.4$ is determined from the S(290 K) value and its correlation with the hole concentration in Ref. 1. Band calculations [16–18] and photoemission experiments [19] show that HTSC has an approximately cylindrical Fermi-surface for electrons in the CuO_2 planes. An ordinary metal with such a simple band is expected to have S_d linear in T. Someone might argue that HTSC is not an ordinary metal and the positive S_o might originate from unconventional Fermi-liquid-likeness of HTSC. The observed development of negative S_o in the heavily-overdoped region where HTSC behaves more like an ordinary metal, however, seems to indicate that the non-zero S_o is from some extra contribution in S rather than unusual S_d.

Superconductivity has its origin at attractive electron-electron interactions which are mediated by some excitations interacting with electrons. The stronger interaction between electron and the excitation generally induces the higher superconducting-transition temperature. Thus it would be never surprising for HTSC to show a large excitation-drag thermopower, revealing the presence of strong interactions between electron and excitations. The most ordinary excitation which drags electrons is phonon. Several authors have tried to explain S of HTSC in terms of phonon drag. Early arguments, however, had some difficulty in explaining the unusual linear T-dependence of S which persists up to 600 K [20,21]. Recently Trodahl [22] has shown that inclusion of phonon drag and a cylindrical Fermi-surface can explain the unusual T-dependence within a conventional Fermi-liquid theory. In the picture, the observed thermopower is a sum of a negative S_d varying linearly in T and a positive phonon-drag thermopower S_g varying little in T above 100 K. The zero-offset S_o is simply the saturation value of S_g. The observed correlation between S_o and the doping-level is attributed to competition between two contributions with opposite sign in S_g; positive for the contribution from the Umklapp processes of electron-phonon scattering and negative for that from the normal processes. The competition between the two contributions is settled by the contour of the Fermi surface which varies with the doping. As the hole doping is enhanced, the cylindrical hole-like Fermi-surface of HTSC expands out and consequently the positive S_o at low doping-levels decreases and becomes zero at some critical doping-level. Extending the argument above the critical level, one might expect that the Fermi surface ultimately turns electronlike and S_o becomes negative. This expectation appears to agree qualitatively with our observations.

Nevertheless we note that phonon is not the only excitation which can generate a drag thermopower and that the Trodahl's argument is not limited only for phonon drag. It can be extended to other excitations interacting with conduction electrons, such as magnon. It is not even certain for high-T_c cuprates whether phonons interact so vigorously with electrons. It is well known for high-T_c cuprates that strong electron-electron interactions induce large AFM spin-fluctuations in both semiconducting and superconducting samples. Many physicists now believe that strong interaction between electron and the spin-fluctuations (quantum of which is paramagnon) is responsible for the high-T_c superconductivity. Therefore it could be a hasty conclusion to claim without extra evidences that phonon is the excitation.

We now examine correlation between excitation drag and the observed S change below T_N in the semiconducting samples, even if similar effects don't have to work on both semiconducting and superconducting samples. Phonon-drag thermopower does not appear to fit in well with the observation. When phonon is the dominant excitation interacting with electrons, S_g is not expected to change substantially in association with the AFM transition. It is because the electron-phonon scattering rate is not significantly affected by the antiferromagnetic electron-spin-ordering transition. Unlike for phonon, AFM ordering suppresses spin-fluctuations and thus paramagnon-drag thermopower is reduced below T_N. The S charge in Fig. 1 is quite similar to that observed in MnTe [23], which has been attributed to the paramagnon-drag effect. Nevertheless, it is not easy to explain why strong electron-paramagnon interaction effects would come out vividly only in S, but not in ρ. The absence of strong T-dependence of S above T_N associated with critical slowing down is another question to be answered for admission of paramagnon-drag thermopower in the semiconducting samples.

Charge carriers in semiconducting high-T_c cuprates are known to be both strongly correlated and severely localized. S_d in such a system may have, in addition to the usual energy-transport term, a spin-entropy term which may reach to several hundred μV/K. [24] Liu and Emin [25] has shown that magnetic ordering reduces the spin-entropy part so effectively, because the exchange interaction between the carrier and the magnetic sites limits the energetically allowable spin configurations. The spin-entropy part can be easily reduced in the presence of a large applied magnetic field as well. Presence of a sizable spin-entropy part in S thus can be ascertained from measurement of magnetothermopower. Early measurements [26,27] expose that S of superconducting samples is almost independent of a magnetic field up to 30 T. Magnetothermopower data for semiconducting samples have not been provided yet.

In summary, we have studied S of La_2CuO_{4+z}, Nd_2CuO_{4-y}, and $Bi_2Sr_{2-x}La_xCuO_{6+z}$. For La_2CuO_{4+z} and Nd_2CuO_{4-y}, S shows an anomaly at T_N, whereas ρ does not. For $Bi_2Sr_{2-x}La_xCuO_{6+z}$, the zero-offset S_o

is found to become negative above some critical doping-level. The development of negative S_o in the overdoped region looks qualitatively compatible with the excitation-drag argument for a system with a cylindrical Fermi-surface. For the origin of the anomalous change in S below T_N, paramagnon-drag and spin-entropy contributions have been considered. We suggest magnetothermopower measurement for probe of spin-entropy part in S of semiconducting samples.

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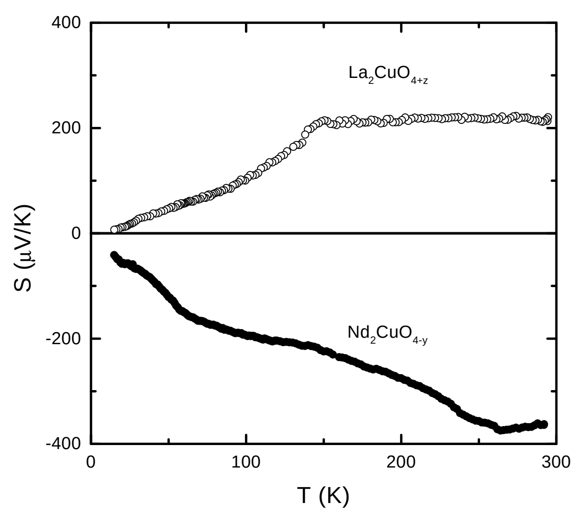

FIG. 1. Temperature dependence of the thermopower for La_2CuO_{4+z} and Nd_2CuO_{4-y}.

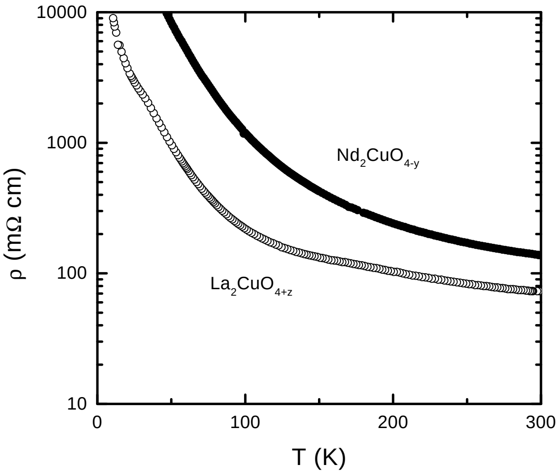

FIG. 2. Temperature dependence of the resistivity ρ for La_2CuO_{4+z} and Nd_2CuO_{4-y} polycrystalline samples.

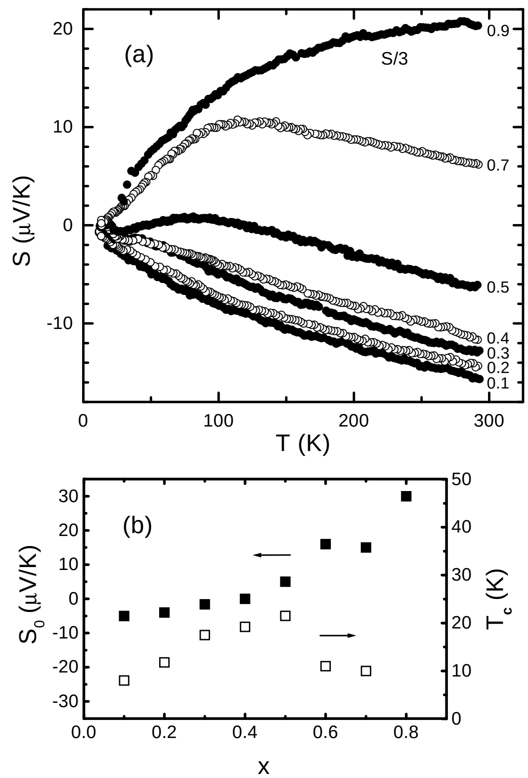

FIG. 3. (a) Temperature dependence of the thermopower of $Bi_2Sr_{2-x}La_xCuO_{6+z}$. The numbers near the curves denote the lanthanum concentration x. The magnitude of the thermopower of the sample with x = 0.9 is scaled down. (b) shows the La-concentration dependence of the zero-offset thermopower S_o (solid squares) and the superconducting-transition temperature T_c (open squares).